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Stormwater Suspended Solids and Pollutant Concentrations in an Urban Stream

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Abstract The chemical and ecological quality of small rivers or streams is not normally classified, but any urban stormwater discharges will result in their impairment. To assist in understanding the resulting applied environmental stress to benthic communities, the empirical relationships between in-stream suspended solids and metal pollutants, initially identified by principal component analysis, are explored using data from a small urbanised upland catchment. When data are amalgamated from individual storms, a correlation for each metal pollutant with suspended solids is obtained, starting very strongly, and decreasing in the order $Fe > Al > Mn > Pb > Cr > Zn > Cu > Ni$. Comparison of pollutant/solids correlations for individual storms is, for some metals, excellent, but differing intercepts and/or gradients can be obtained for an individual metal between storms. The practice of assessing their correlation based on event mean concentrations or longer-term averages across several storm events may conceal strong correlations for individual storms, exemplifying the impact of variable

catchment characteristics and storm conditions; Cd and Be are poorly correlated with suspended solids and are likely affected by changes in background pollution levels. The analysis of covariance also highlights a significant difference between certain storm events for specific metals, which calls into question the validity of using combined storm-event datasets. The relationships identified here enable the determination of stormwater pollutant loads from suspended solids concentrations for heavy metals and are useful for developing water quality assessments.

Keywords Heavy metals · Pollution · Stream · Stormwater · Suspended solids · Water quality

1 Introduction

Protection for all surface water bodies in Europe is afforded under the Water Framework Directive (2000/60/EC), established by the European Union and implemented into UK Law under The Water Environment Regulations 2017 (Statutory Instruments Legislation SI 2017/407). This is designed to ensure that good quality status is achieved by 2027. As only 40% of rivers in Europe and 14% of rivers in England are currently reported to have good ecological status, considerable improvement is vital (European Environment Agency (EEA) Report 7/2018; EAC 2022).

The EU Biodiversity Strategy for 2030 and the 2021 Environment Act Legislation (2021) established by the UK Government require that the decline

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of domestic species be halted by 2030. This ensures that targets to improve surface water quality and protect the benthic species they hold are legally binding, emphasizing the national and international importance of this issue (European Commission, Directorate-General for Environment, 2021; EAC 2022).

Attention here is focused on small rivers and streams — their water quality is not routinely assessed, although they are important for recreational use. They can also influence downstream water quality as they drain the sub-catchments for larger water bodies. Many have been urbanised and utilised for the routine disposal of untreated stormwater via separate surface water sewers along their urban length. It has been recognised for some time that urban stormwater is a major cause of impairment of receiving waters (e.g. Ellis & Hvitved-Jacobsen, 1996).

The nature of pollution in stormwater is complex, but it can be simplified into six parts: suspended sediment, heavy metals, biodegradable organic matter (as defined for example by biochemical oxygen demand (BOD) and chemical oxygen demand (COD)), organic micro-pollutants (e.g. PAHs and PCBs), pathogenic micro-organisms, and nutrients (Hvitved-Jacobsen et al., 2010).

Suspended solids and heavy metals are under focus here, with the former considered to be a primary pollutant source and a sink. Solid particulate matter has been widely used as an environmental indicator and plays an important role in the assessment of metal contamination (Beck & Birch, 2012; Drygianiaki et al., 2020; Fan et al., 2021; Soares et al., 1999; Zuliani et al., 2022). Many contaminants are more concentrated in solid matter than in the water column; hence, the suspension of solids during high flows can greatly increase toxicity (Christensen et al., 2006; Rügner et al., 2019). Metal pollutants are associated with solids via numerous binding forms: mobile (exchangeable and carbonate-bound), potentially mobile (Fe–Mn oxide-bound and organic matter/sulphide-bound), and residual (Baran & Tarnawski, 2015).

Increased imperviousness and the removal of riparian vegetation associated with urbanisation are the main factors which contribute to increased stormwater runoff into urban streams and encourage a surge in pollutant suspension (Calderon et al., 2019; Robson et al., 2006). This increase in stormwater runoff

can also be correlated with a larger input of solid particulates and their associated heavy metals from both lithogenic and anthropogenic sources, leading to greater stress on river ecosystems (Ateş et al., 2020; Goldyn et al., 2018; Zhang et al., 2018).

The risk posed by pulse exposures of physical and chemical stresses from storm events to benthic communities is difficult to evaluate, being influenced by organism sensitivity, duration and frequency of pollution pulses (Burton & Johnston, 2010), and synergies between pollutants. A more detailed knowledge of pollution pulse characteristics would inform such studies (e.g. Ashauer et al., 2007), but predicting pollutant concentrations and loads reliably continues to be one of the greatest challenges in urban hydrology (Fletcher et al., 2013; Murphy et al., 2015). High-quality spatial and temporal data are critical factors in predicting pollutant loads, as without local data, models cannot be tested or used successfully (Vaze & Chiew, 2003). Model calibration and verification are also often sensitive to the specific data sets used, making the collection of more reliable field data a priority (Bertrand-Krajewski, 2007).

Field data are often presented in terms of event mean concentrations (EMCs) or sometimes as averages over much longer time periods to evaluate the impacts of urban stormwater on receiving waters. However, simplifying the variability in metal concentrations by sampling sporadically over multiple storm events is likely to reduce the accuracy in modelling pollutant exposures and limit the viability of stormwater management solutions (Bağ et al., 2019; Vaze & Chiew, 2003). The behaviour of pollutants within and between individual storm events is examined in this study, using one catchment to eliminate any influence of variation in land use and other localised factors such as regional geology, elevation, and meteorological conditions (Bağ et al., 2019; Gellis, 2013; Shi et al., 2019).

Therefore, this study aims to gain a greater understanding of the relationship between suspended solids and metal pollutants during storm events, collected from an ordinary watercourse with sub-standard ecological quality; by examining the correlation of heavy metals to suspended solids, controlled, both by internal river characteristics and the source of external pollutant inputs, it may be possible to establish a more realistic frequency distribution of biotic exposure. Ultimately, this can then be related to the

presence or absence of benthic organisms over their lifecycle within the river and be used to determine the scale and type of remediation required.

This paper is organised as follows: Section 2 details the methods and materials used in the collection of river discharge data, heavy metal concentrations, and physiochemical water quality parameters. Section 3 presents the results of that data: storm characteristics followed by the statistical analysis of heavy metals, suspended solids, and water quality parameters; both are interpreted, and the implications of the latter are considered with respect to the wider literature. Finally, the conclusions are discussed in Section 4.

2 Methods and Materials

This study utilises a 3.871 km² catchment to the north of Sheffield, South Yorkshire, UK (Fig. 1).

Land use classes include woodland (32.6%), grassland (33.2%), arable and horticultural land (8.3%), and medium-density suburban housing (25.8%). The underlying geology comprises a Carboniferous sedimentary sequence of coal measures, mudstones, siltstones, and sandstones (British Geological Survey, Geology of Britain Viewer, n. d.). The average slope, as measured between two points located at 10% and 85% of the main stream length, is 36.4 m/km. A number of tributaries in the western rural area drain into an ordinary watercourse (Charlton Brook) in a green corridor of high amenity value within the urbanised area. Surface water outfalls discharge to the Charlton Brook along its urbanised length; the area connected to the surface water drainage network is estimated to be 0.524 km² with the remainder of the urban area draining to outlets outside the catchment boundary. There are no combined sewer overflows, but there is visual evidence of polluted surface water outfalls.

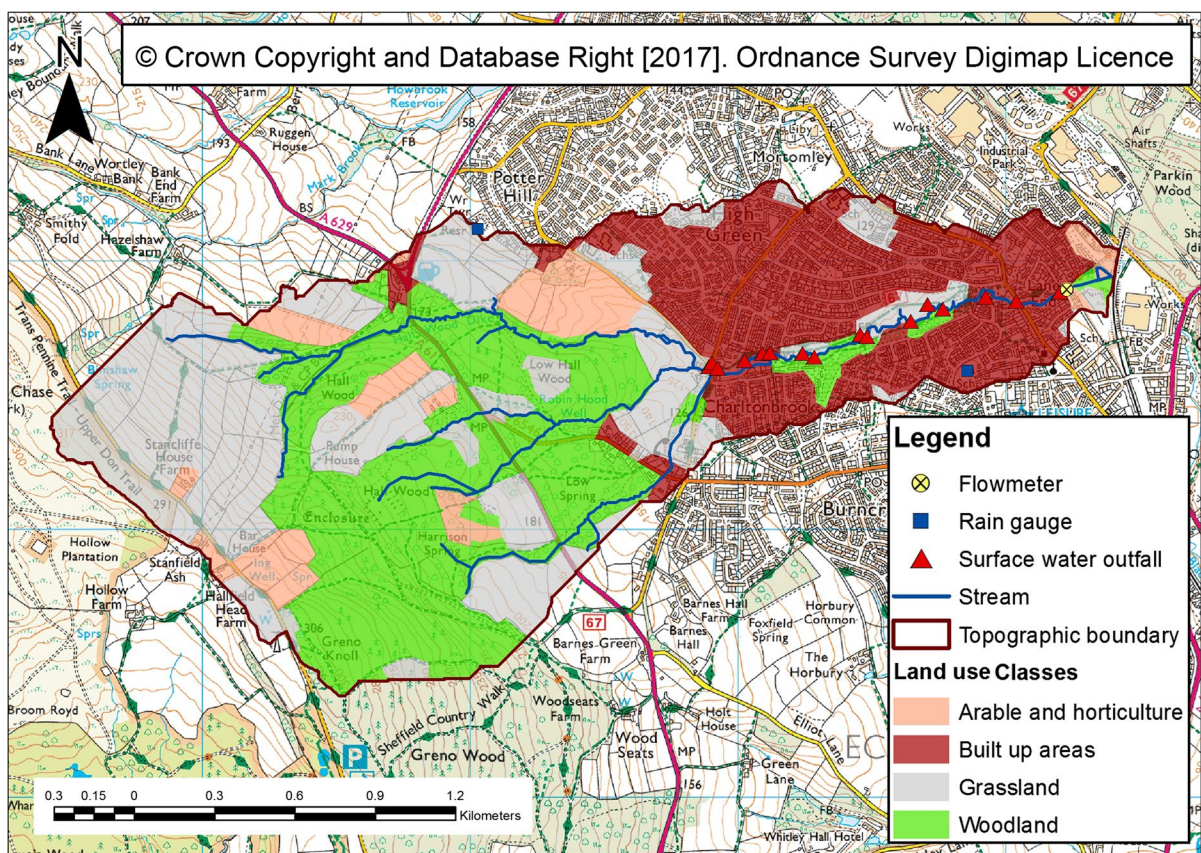


Fig. 1 Land use and catchment boundary for the Charlton Brook based on topographic divide

Charlton Brook has background levels of water hardness from 136 to 140 mg/L (Robson et al., 2006) and discharges into the Blackburn Brook, a water body that flows into the River Don in the Humber River Basin District. Blackburn Brook currently has a moderate ecological status and good chemical status (at the end of the 2015 Cycle 2), with the objective of good status in both these assessments being achieved by 2027 (Environment Agency, 2017; EAC 2022).

Discharge is measured near the end of the catchment (Fig. 1) at Ordnance Survey NGR SK 3524 9691 using an ultrasonic velocity and depth meter (STARFLOW™) with a logging frequency of 5 min. The meter is mounted on a steel frame spanning between the walls of a 0.92 m radius semi-circular stone arched railway culvert. Velocities were occasionally intermittent, and therefore a stage-discharge relationship was determined by dilution gauging with constant injections of fluorescent dye via a Mariotte vessel. Rhodamine WT dye concentrations were determined using a Series 10 Turner Designs fluorometer. A tipping bucket rain gauge was located at Potter Hill (SK 3304 9712), and its performance was confirmed by a nearby Snowdon daily rain gauge. A further gauge was mounted on the roof of Lound School (SK 3486 9659).

For this work, seven storm events were sampled for heavy metals and suspended solids, together with the general chemical water quality parameters of dissolved oxygen (DO), pH, BOD, COD, and ammonia (NH₃). The metals investigated were selected on the basis of their inclusion on lists of dangerous substances discharged into the aquatic environment (European Council Directive 76/464/EEC, 1976): Cd, Be, Cu, Cr, Fe, Pb, Ni, and Zn, with the inclusion of Al and Mn due to other water quality criteria (e.g. United States Environmental Protection Agency (USEPA), 1986). The measured water quality parameters have all been observed to affect hydrological conditions and, consequently, have the potential to impact heavy metal concentration (Huang et al., 2017; Komínková, 2012; Shine et al., 1998; Soto-Varrel et al., 2015). The number of events recorded was governed by the available sampling period and the success of capturing storm events on-site by anticipating rainstorms from Met Office radar data. Hand-held meters were used to measure pH, dissolved oxygen, and temperature in the field. River water samples were collected manually into 2 L polypropylene bottles. Analyses of suspended solids, ammonia, COD,

and BOD followed the procedures of the Standing Committee of Analysts (1980, 1981, 1986 and 1988).

Metal concentrations were established from 100 mL samples filtered using Whatman 0.45 µm Membra-Fil filters and acidified by the addition of 2% nitric acid (Aristar grade). The preliminary metal analysis was carried out using a Spectroflame Model-P™ Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Calibrations were carried out using standards of 5, 20, and 100 ppm. Metals found to be below the limit of detection were tested under Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), using a Hewlett Packard Agilent 4500 Mass Spectrometer, with calibration standards of 0, 100, 200, and 500 ppb.

3 Results and Discussion

3.1 Storm Characteristics

The characteristics of the measured storm events are shown in Table 1. Each antecedent dry weather period (ADWP) is similar with a mean value of 3.5 days, and total rainfalls are modest. Modal storm duration and peak intensity are about 1.5 h and 6 mm/h, respectively, with Storm E being four times as intense and with a shorter storm duration of 0.58 h. The frequency distribution of maximum storm discharge, calculated from flow monitoring records over an extended period (Fig. 2), indicates that the majority of measured storms are common events.

The hydrograph tail is long; Fig. 3 illustrates the first 5 h of a hydrograph, but a further 6.5 h pass before the recession curve of baseflow is reached. Using an arithmetic mean of data from the two rain gauges (Fig. 1) and a linear increase in baseflow over the duration of the run-off, the percentage run-off for the catchment upstream of the flowmeter is 3–6% for singular storm events. This is likely to be an underestimate, as approximately 50% of the urban area, largely in the northern part of the suburbs, is not served by the separate sewers that discharge into Charlton Brook.

Flow measurement in the rural area and hydraulic modelling indicate that urban stormwater from the suburban area causes the first peak on the hydrograph (Fig. 3) due to its shorter time of concentration if the areal rainfall is uniform; the second peak with the

Table 1 Rainfall and stream stormflow characteristics for six rainstorms, A–F, in the Charlton Brook catchment between 4 March and 29 July 2003. The 1st and 2nd refer to the order of peaks observed in a hydrograph or in the distribution of suspended solids

Event	ADWP days	Total rainfall depth mm	Storm Duration hrs	Peak intensity mm/hr	Duration of peak intensity min	Runoff %	Element	Background values L/s and mg/L	Time to peak, T _p hrs	Maximum event value L/s and mg/L	Time base hrs
Storm A: 04/03/03	2.64	2.21	1.64	6	2 bursts, Each 2'	3.25	Discharge	Start 39.6	1st 1.08	1st 64.5	11.5
								End 42.4	2nd 2.58	2nd 54	
Storm B: 01/04/03	3.86	3.09	1.67	3	33	–	Discharge	Start 3.87	0.83	110.3	3.92
								End 3.67	1st 1.02	1st 55.0	
Storm C: 24/04/03	0.066	1.85	1.58	2	2	–	Discharge	Start 24.8	2nd 2.92	2nd 50.1	≈12.75
								End 28.6	1st 1.00	3rd 62.8	
Storm D: 27/06/03	3.21	2.80	1.53	6.0	2 bursts: 10' and 5'	Overall 3.73	Solids	Start 9.5	1st 1.00	1st 123.5	15.75
								End -	2nd 70.5		
Storm E: 21/07/03	4.13	6.60	0.58	24.0	3	–	Discharge	Start 11.0	1st 0.58	1st 50.7	12.08
								End 12.1	2nd 2.67	2nd 38.0	
Storm F: 29/07/03	3.96	4.7	2.92	3.0	2 bursts Each 8'	5.53	Discharge	Start 38	0.75	300	–
								Start 5.5	1st 1.58	65.0	
Storm G: 29/07/03	4.13	6.60	0.58	24.0	3	–	Solids	Start 2.66	1.17	59.7	2.17
								Start 15.4	1st 0.50	187.9	
Storm H: 29/07/03	3.96	4.7	2.92	3.0	2 bursts Each 8'	5.53	Discharge	End 1.58	2nd 1.58	2nd 75	14.42
								Start 4.9	0.33	50.1	
Storm I: 29/07/03	3.96	4.7	2.92	3.0	2 bursts Each 8'	5.53	Solids	Start 10.6	1st 1.17	1st 34	2.33
								End 25.3	2nd 2.75	2nd 24	

Fig. 2 Frequency distribution of peak storm flows (01 March 2002 to 20 January 2004)

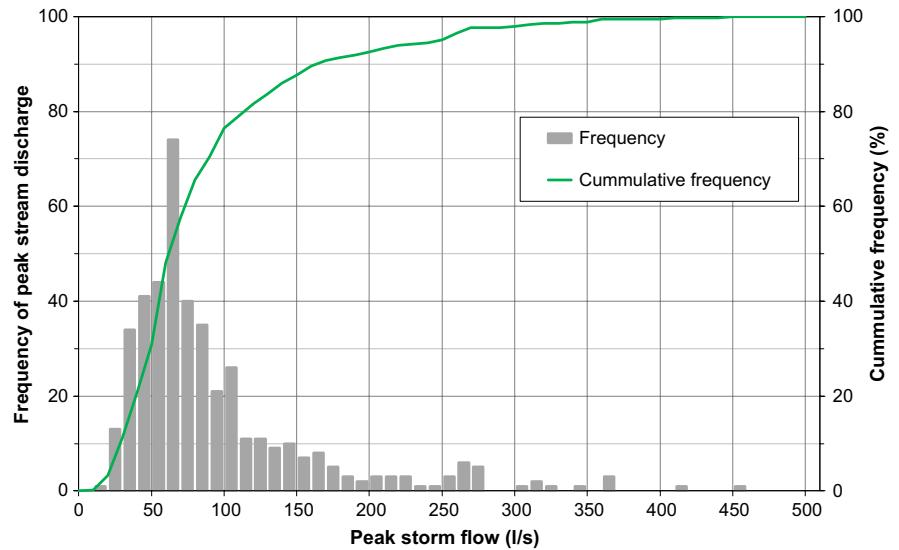
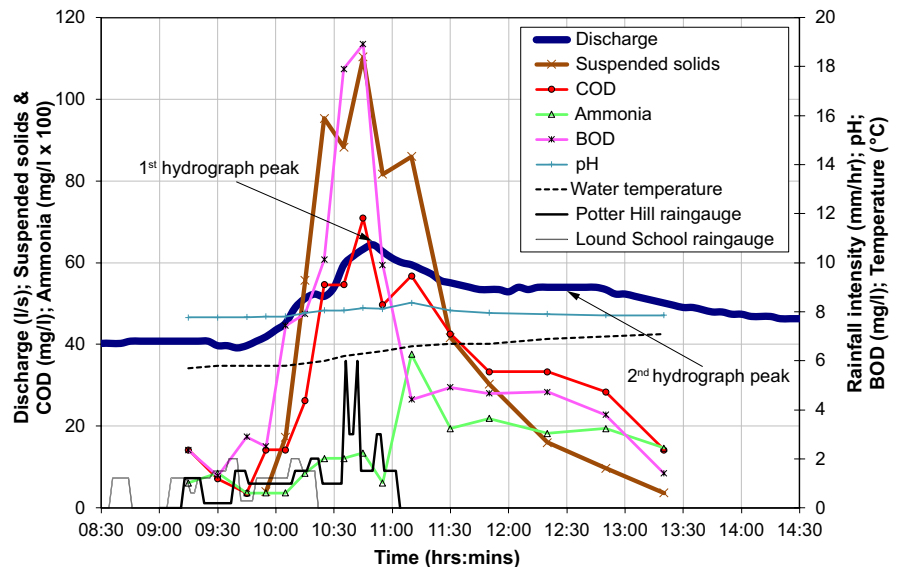


Fig. 3 Hydrograph and water quality; Storm A

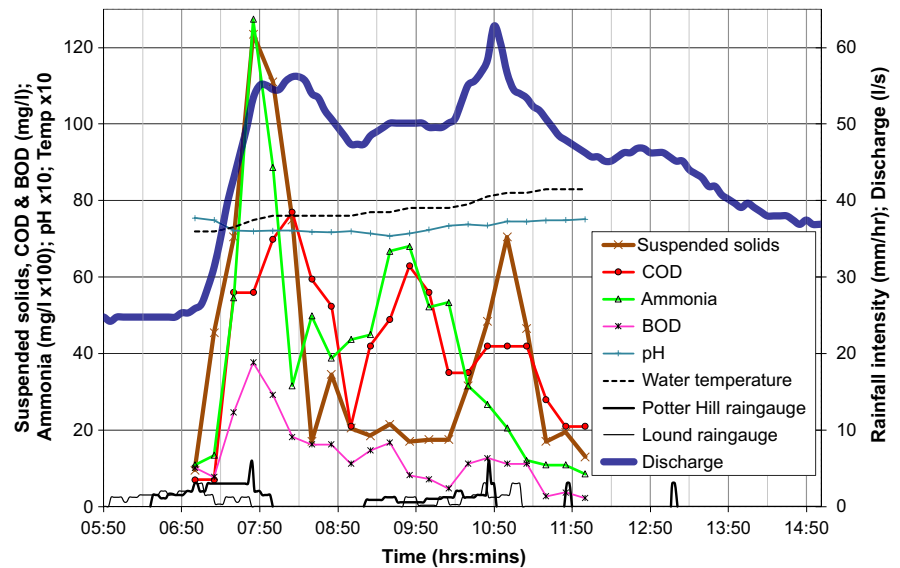


shallower temporal gradient is largely due to green field run-off from the upstream rural land use (Robson et al., 2006). Multiple rainfall events with short intervening dry weather periods result in the superposition of hydrographs; hence, multiple distinct peaks of discharge are observed (Fig. 4; Table 1).

The differing origins of stream water influence the magnitude of the chemical variables. The temporal distributions of BOD and COD during the measured storm events are similar to the patterns observed for suspended solids, but the COD/BOD ratio varies

within and between storms. Observed ammonia concentrations are not consistent between storms; concentrations associated with the first peak discharge originating from urban stormwater are larger compared to those of rural origin for one storm (Fig. 3), and yet, the opposite behaviour is also observed in another hydrograph (Fig. 4); it appears the available ammonia can be exhausted when the intervening dry weather period between storms is short.

Background concentrations of suspended solids in the baseflow for this upland stream are low

Fig. 4 Hydrograph and water quality; Storm B

(4–10 mg/L; Table 1). The ADWP is similar for some of the measured storms (Table 1); any variations are not anticipated to impact the quantity of solids available for suspension following observations elsewhere (Brodie & Dunn, 2010), as loads are expected to reach equilibrium values over several dry days (Vaze & Chiew, 2003; Zhang et al., 2018).

There is a small lag in the rise of suspended solids concentrations compared to the initial rise in storm flow. Peak suspended solids and peak flow occur at similar times. For the first peak of urban runoff, hysteresis in the plot of discharge versus suspended solids concentration is clockwise if the timing of both the peak discharge and suspended solids are the same or if the suspended solids peak precedes that of the discharge. This is also observed by Gellis (2013) and Haddadchi and Hicks (2020). On three occasions (Storms B, D, and F), further rainfall increases both the discharge and solids concentrations and indicates that whilst the sources of particulate solids are not exhausted, they are limited, as the quotient of the second peak suspended solids to discharge is smaller (Fig. 4). How much of the available catchment store of solid matter is mobilised during a storm event will depend on the nature of the rainfall; as might be expected, the largest suspended solids concentration is observed with the storm of shortest duration and largest total rainfall (e.g. Nadal-Romero et al., 2008). The pattern

observed for other storms is not immediately apparent (Table 1); a number of other variables such as rainfall intensity, depth, and river flow have been identified as influential (Brodie & Dunn, 2010; Zhang et al., 2018). Furthermore, the dilution of suspended solids entering the stream will be greater during wetter seasons due to higher baseflows and larger runoff volumes (Brodie & Dunn, 2010; Deng et al., 2018).

Various relationships can be explored to predict the maximum concentration of suspended solids, which is relevant to the later discussion of its relationship to metal concentration exposure; the strongest correlation ($r^2=0.947$) is obtained with the regression of the dependent maximum suspended solids concentration for the first peak minus the background concentration, on the independent reciprocal of the time to peak discharge, which is a function of effective rainfall and catchment characteristics. The derived relationship (gradient = 204.1 mg/L h, intercept = -95.42 mg/L) may be relevant only to the frequency of these measured storms and to similar catchments, as the availability of solids will vary (e.g. Gellis, 2013). Partial event mean concentrations (Lau et al., 2009), calculated for the duration of discrete suspended solids concentration distributions when a return to the background concentration is obtained, range from 30 to 140 mg/L.

3.2 Statistical Analysis of Heavy Metals, Suspended Solids, and Water Quality Parameters

Data were analysed using the statistical analysis software jamovi (The jamovi project, 2022). Principal component analysis (PCA) with Varimax rotation was applied to explore initial affiliations between the measured water quality parameters, suspended solids, and heavy metals. Data were centred and standardised prior to PCA to avoid variable bias. Quantile–quantile plots (Q–Q plots) find the temporal distribution of most variables to be skewed (e.g. Figure 3), caused by a number of possible factors, including the concentration of the urban area near the sampling point and the mechanics of solids and pollutant mobilisation. As the sampling rate was constant during an event, a variable's frequency distribution is likely to be similarly skewed. Numerous lower concentrations also exacerbated this issue, hence only a single background sample prior to storm runoff, and at the end (if available) was included in the dataset. In some research, such data are transformed prior to analysis in order to obtain normal (Gaussian) distributions, or distributions that are close to normal (e.g. Sojka et al., 2018), whilst others have used raw/scaled data (Tauler et al., 2009) or both (Ho et al., 2010; Nguyen Van et al., 2016). Here, both standardised and transformed data (using natural logarithms) are plotted (Fig. 5). Storm B was set aside due to the absence of Fe, Al, Mn, and Be data; similarly, Cd was not considered for PCA due to its absence from Storm E. Bartlett's test of sphericity identifies significant redundancy between variables ($p < 0.001$), and the overall Kaiser–Meyer–Olkin (KMO) sampling adequacy value is > 0.7 ; hence, the use of PCA is appropriate.

A correlation matrix was calculated, comparing all measured variables using Pearson correlation coefficients. Because the majority of the correlation coefficients are higher for the untransformed data, the transformed data were set aside. A coefficient ≥ 0.8 represents a very strong correlation, ≥ 0.7 is a strong correlation, < 0.7 and ≥ 0.4 is a moderate correlation, and < 0.4 is a weak correlation (Ho et al., 2010; Singh et al., 2011). Linear regression was undertaken using untransformed data.

Analysis of covariance (ANCOVA) was used to evaluate whether the mean concentration of a storm metal concentration was equal for different storm events, whilst statistically accounting for both

suspended solids concentrations and the interaction effect between the storm event and suspended solids. Post hoc Tukey tests were used to compare storm means, with significance determined at $p < 0.05$. Storm B data were not included due to the absence of four metals. Departures from normality for residual concentrations of both metal and suspended solids were largely resolved by transformation using natural logarithms. Any departure caused by occasional large outlying concentrations (defined as being three standard deviations from the mean) was resolved by their removal.

3.2.1 Principle Component Analysis Results

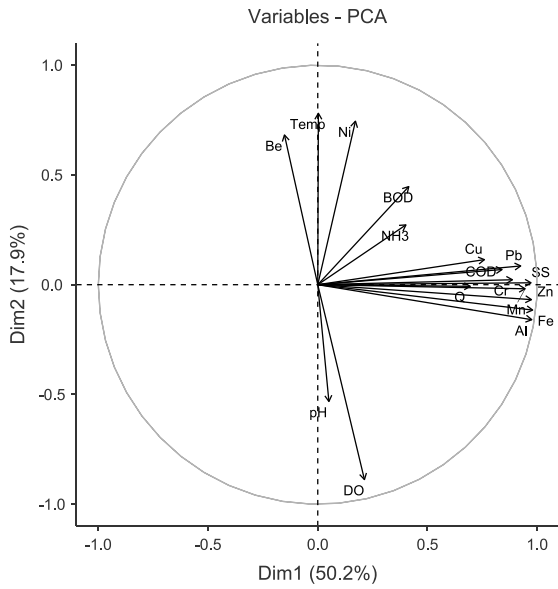
The results of the PCA tests are displayed in Table 2 and Fig. 5. Both the standardised and the standardised transformed data have similar values of total variance accounted for by the first four PCs (50, 18, 11, 6% and 46, 18, 10, 7% respectively), and the eigenvalues are greater than one (8.53, 3.05, 1.83, 1.10 and 7.82, 3.14, 1.63, 1.22 respectively).

Most metals, suspended solids (SS), COD, and the stream discharge (Q) are strongly positively associated with principal component one (PC1), with higher loadings for the untransformed data. Be, Ni, and temperature (Temp) are positively associated with PC2. Ammonia (NH_3) and pH loadings are highest for PC3 and PC4 respectively and thus do not make a strong contribution to metal concentrations (Table 2).

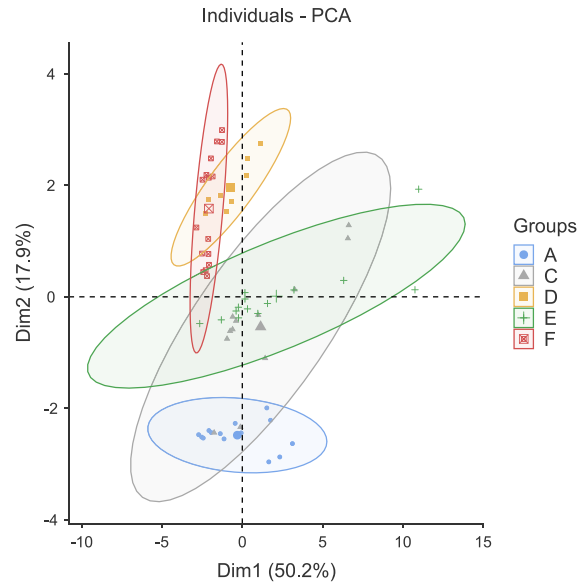
The PCA group plot with untransformed data (Fig. 5b) shows that data from Storms C and E are clustered together and are mostly associated with PC1. Storms D and F are clustered and positively associated with PC2, with their mean values negatively associated with PC1. Storm A is negatively associated with both PC1 and PC2. Transformation distributes data more evenly over the group plot and reduces the spread of Storms C and E which improves their similarity. Storms A and D also have a greater association with PC1. Storm D overlaps with all storms apart from Storm A, which forms a distinct cluster. Therefore, whilst transformation may improve the normality of variable frequency distributions, it also alters correlations and relationships to the PCs.

Overall, PCA tests show there is a close association between suspended solids and the majority of heavy metals when observing a combination of the variables. They also identify that except COD, the measured

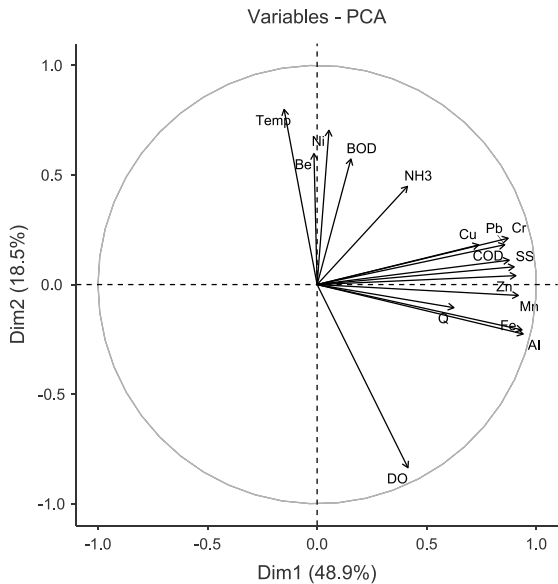
a) PCA biplot showing standardised variable contributions to PC1 and PC2



b) PCA scatter plot showing the arrangement of standardised individuals by storm event



c) PCA biplot showing transformed variable contributions to PC1 and PC2



d) PCA scatter plot showing the arrangement of transformed individuals by storm event

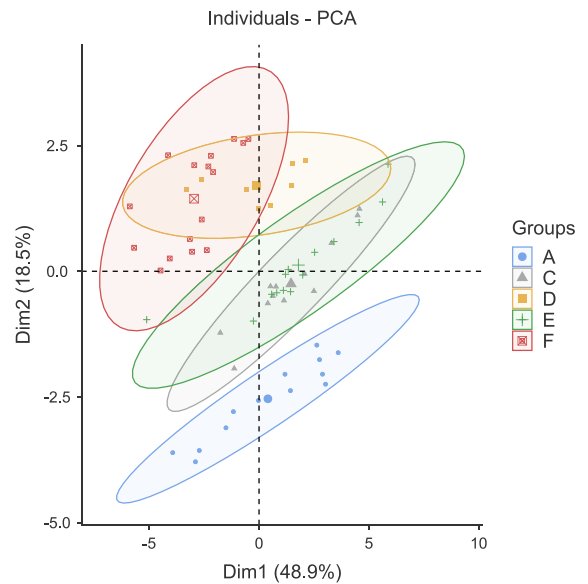


Fig. 5 PCA biplots and scatter plots

Table 2 Component loadings (values below 0.3 not shown)

a) Standardised data						b) Standardised and transformed data					
PC	1	2	3	4	Uniqueness	PC	1	2	3	4	Uniqueness
Q	0.828		-0.335		0.1183	Q	0.648			-0.323	0.3703
SS	0.909		0.35		0.0482	SS	0.837		0.382		0.089
Cr	0.92				0.1113	Cr	0.902	0.339			0.0495
Ni		0.78	0.348		0.2577	Ni		0.626	0.566		0.2858
Cu	0.751				0.4014	Cu	0.772				0.3502
Zn	0.941				0.0352	Zn	0.923				0.0942
Pb	0.92				0.1218	Pb	0.876				0.1777
Fe	0.937				0.0263	Fe	0.904	-0.337			0.0603
Al	0.927				0.0174	Al	0.904	-0.319			0.0441
Mn	0.986				0.0265	Mn	0.941				0.1056
Be		0.847			0.2538	Be		0.84			0.1949
BOD		0.37	0.681		0.3299	BOD			0.837		0.2905
COD	0.679		0.669		0.0433	COD	0.826		0.34		0.1069
DO		-0.729		0.493	0.1527	DO	0.399	-0.494	-0.39	0.592	0.0952
pH				0.832	0.2434	pH				0.82	0.3245
NH ₃			0.869	-0.318	0.1055	NH ₃	0.329		0.66	-0.406	0.2526
Temp		0.722		-0.489	0.1885	Temp		0.407	0.31	-0.652	0.2969

water quality variables are weakly associated with PC1 and, consequently, the majority of heavy metal concentrations. The significant overlap between certain storm events but not others also highlights an inter-storm variability that may be caused by spatial and temporal changes in the availability of the individual variables themselves.

3.2.2 Correlation Matrix Results

To support the PCA, a correlation matrix is presented (Table 3). Variables are better correlated with suspended solids (SS) than with Q. There are high correlations amongst SS, Fe, Al, Zn, and Mn, with the strongest occurring between Fe and Al ($r=0.993$). Ni, Be, Cd, DO, and pH, i.e. variables associated with PC2, have insignificant correlations with SS and weaker correlations with each other overall.

In terms of the water quality variables, only COD appears to have a strong relationship with heavy metals, showing strong correlations >0.7 with Fe, Al, Zn, and Pb. This is supported by the PCA analysis, where COD has a significant loading with PC1.

3.2.3 Linear Regression Results

The relationship between metal pollutants and suspended solids concentration is examined further using linear regression shown visually in Figs. 6 and 7 and in Table 4, both as individual storms, and relationships pooling all storm data for each individual pollutant. Metals are discussed in order of the strength of their correlation with suspended solids.

Aluminium and Iron There is a very strong positive correlation between suspended solids and aluminium for the runoff in Storms A and C and an even stronger correlation for Storms D and E. The gradients are similar for three of these Storms, with Storm A's being slightly larger (Fig. 6; Table 4). Storm F is the exception, with the slope being about a third of the other runoff and with greater scatter; the cause of this behaviour is unclear, as the characteristics of both storm and stream responses are similar to Storm D.

The regression line (Fig. 6) for the pooled Al has a very strong correlation despite fluctuations in gradients between individual storms. Similar trends are also present for iron.

Table 3 Correlation matrix of all measured variables

Q	SS	Cr	Ni	Cu	Zn	Cd	Pb	Fe	Al	Mn	Be	BOD	COD	DO	pH	NH ₃	Temp
Q	—	***		***	***		***	***	***	***		***	**			***	*
SS	0.641	—	***	***	***		***	***	***	***		***	***			***	
Cr	0.651	0.825	—	***	***		***	***	***	***		***	***				
Ni		0.268	—			***	*	***	***	***		***	***		*		***
Cu	0.567	0.695	0.599	—	***		***	***	***	***		*	***			*	
Zn	0.648	0.921	0.886	0.753	—		***	***	***	***		**	***	*		*	
Cd			0.735			—	*	*	*	*			***	***	***		***
Pb	0.638	0.847	0.93	0.664	0.919	0.286	—	***	***	***			***			*	
Fe	0.662	0.971	0.854	0.687	0.955	-0.29	0.877	—	***	***		**	***	*		**	
Al	0.631	0.961	0.868	0.669	0.958	-0.32	0.880	0.993	—	***	*	**	***	**		**	
Mn	0.82	0.907	0.914	0.692	0.917		0.904	0.924	0.914	—		*	***	***		***	
Be			0.573			0.642			-0.25		—	*	*	***		***	***
BOD			0.393	0.292	0.359			0.392	0.38	0.247		—	***	*		***	
COD	0.379	0.859	0.572	0.624	0.772		0.71	0.825	0.819	0.672	-0.25	0.515	—			***	
DO			-0.49		0.308	-0.53		0.302	0.346		-0.49	-0.3	—		***		***
pH			-0.30			-0.56							0.437	—	***	**	*
NH ₃		0.43		0.298	0.314		0.317	0.35	0.355		0.499	0.482	0.776	—	-0.35	—	—
Temp	0.306		0.359			0.544								-0.8	-0.27	—	—

Values of *r* that are not significant at the 5% level are not shown. Bold values indicate transformed > untransformed coefficients. Storm B data excluded

p* < 0.05; *p* < 0.01; ****p* < 0.001

Fig. 6 Correlation between aluminium and suspended solids concentrations

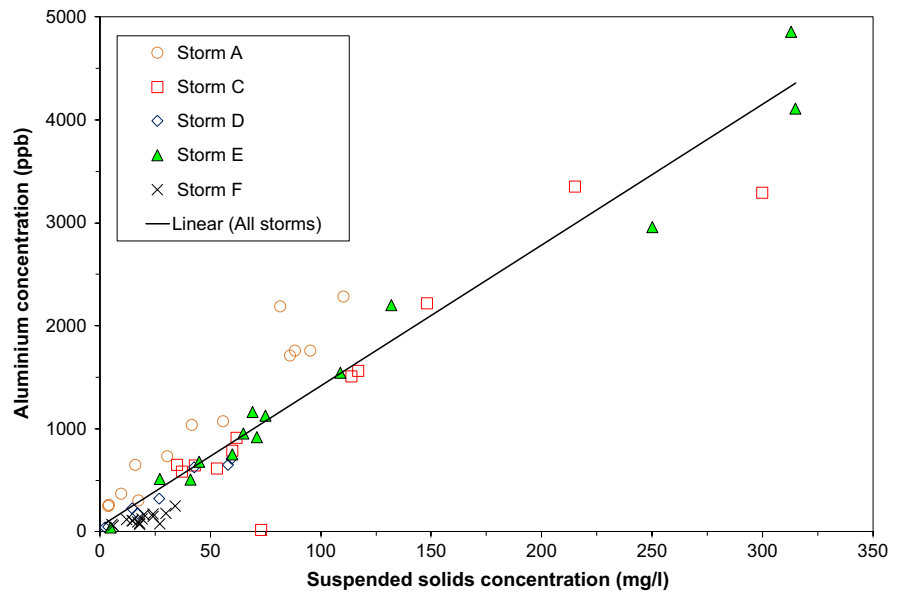
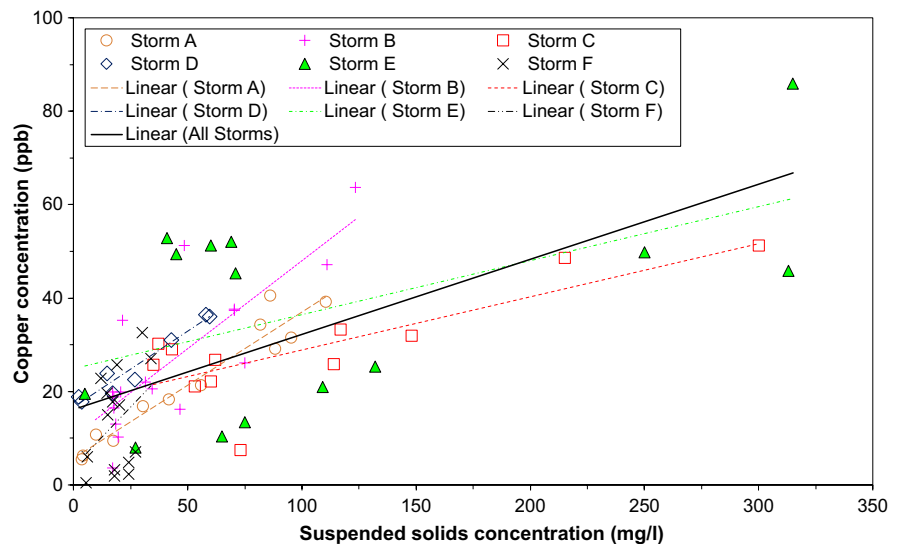


Fig. 7 Correlation between copper and suspended solids concentrations



This very strong positive correlation for Al is replicated in data collected by Goldyn et al. (2018) from the Upper Cybina River in Western Poland (data considered from this study were constrained to before the Antoninek reservoir to preserve a more comparable catchment). An r^2 of 0.978 compares well to the average correlation for Charlton Brook. Fe also very strongly correlates with suspended solids in the Polish catchment, with an r^2 of 0.874 compared to 0.943 for the Charlton Brook. Peraza-Castro et al. (2016) also show a very strong correlation between suspended particulate matter and Fe ($r^2=0.917$) using data collated from numerous storm events in the Oka River catchment, Northern Spain.

The very strong correlation between Al and Fe concentrations (Table 3) suggests they have a shared source and/or analogous geochemical behaviour (Fan et al., 2021). That and their consistent relationship with suspended solids can be explained by both metals having a modally lithogenic origin. Recent XRF (X-ray fluorescence) spectroscopy data from rock samples collected within the Charlton Brook catchment (Reynolds, 2022) indicate that iron and aluminium represent two of the three most abundant elements detected. Additional anthropogenic Al and Fe from the soil or as urban and industrial runoff were ruled out

Table 4 Linear regression of suspended solids concentrations (mg/L) and metal pollutants (ppb). Blank cells indicate absent data

Storm event date	Metal ppb	Cr	Ni	Cu	Zn	Cd	Pb	Fe	Al	Mn	Be
Storm A: 04/03/03	Gradient	0.4014	0.0477	0.3137	0.9454	0.0049	0.3949	39.6611	18.7782	4.5607	0.0036
	Intercept	4.461	3.894	5.615	6.873	4.589	6.543	102.625	181.706	40.590	1.238
	r^2	0.961	0.774	0.932	0.954	0.238	0.920	0.950	0.944	0.961	0.518
Storm B: 01/04/03	Gradient	0.3962	0.0905	0.4175	1.1473	0.0047	0.3907				
	Intercept	4.057	4.559	26.080	26.115	0.131	3.033				
	r^2	0.778	0.597	0.554	0.693	0.460	0.828				
Storm C: 24/04/03	Gradient	0.1526	0.0320	0.1134	0.4614	0.0012	0.2349	27.8371	11.9953	2.5554	0.0002
	Intercept	2.133	3.497	17.577	5.508	4.177	1.394	-88.855	175.170	34.965	1.081
	r^2	0.848	0.840	0.626	0.851	0.629	0.772	0.927	0.935	0.832	0.026
Storm D: 27/06/03	Gradient	0.1959	0.0401	0.3261	0.6848	0.0027	0.3561	25.7764	11.8079	3.9049	0.0031
	Intercept	13.988	12.697	16.592	15.366	21.637	28.161	-36.013	18.220	88.534	3.390
	r^2	0.924	0.965	0.944	0.979	0.340	0.843	0.996	0.969	0.957	0.261
Storm E: 21/07/03	Gradient	0.3982	0.0383	0.1156	0.5627		0.3414	29.3452	13.6645	5.4503	0.0001
	Intercept	-7.219	1.383	24.851	5.118		1.962	193.754	55.512	89.583	2.596
	r^2	0.852	0.948	0.293	0.971		0.910	0.990	0.970	0.979	0.0003
Storm F: 29/07/03	Gradient	0.2549	0.0220	0.5066	0.5417	0.1173	0.2344	7.4107	4.9833	2.4718	0.0622
	Intercept	5.228	13.363	3.962	2.132	5.906	4.402	-0.911	27.953	-8.233	2.652
	r^2	0.120	0.467	0.149	0.186	0.040	0.384	0.589	0.571	0.562	0.029
All storms	Gradient	0.2792	0.0159	0.1477	0.5247	-0.0186	0.2833	30.1174	13.6963	4.6221	-0.0041
	Intercept	5.285	7.256	21.102	21.045	6.889	8.199	-43.537	64.489	11.061	2.715
	r^2	0.677	0.068	0.281	0.614	0.020	0.725	0.943	0.924	0.820	0.028

after comparing both metal concentrations in the solid particulates and the rock samples to their concentration in the soil (UK Soil Observatory, UKSO Map Viewer [n. d.](#)); their concentration in the soil versus the rock is not noticeably different, nor is their concentration in the solids versus the soil. Zuliani et al. (2022) also attribute a very strong correlation ($r=0.98$) for Al and Fe concentrations in the Sava River catchment to their large abundance in the Earth's crust.

Al and Fe's very strong correlation with other metals (Zn, Mn, Pb, and Cr) can also be explained by their lithogenic origin. Since a large quantity of suspended solids are sourced naturally, directly from the parent rock or the soil, it is reasonable to assume lithogenic solids, rich in Al and Fe, act as a large sink for other metals in the watercourse (Zuliani et al., 2022). Fe's strong metal correlations could also be associated with Fe-Mn oxide binding in solids (Baran & Tarnawski, 2015).

A lithogenic source is more conducive to a consistent input of metal into the watercourse, encouraging a stable relationship with suspended solids over

multiple storm events. This is in contrast to anthropogenic metals, the concentration of which are controlled by fluctuating human activity such as traffic, agriculture, and industry (Ateş et al., 2020; Miranda et al., 2021). The bonds between lithogenic metals and solids are also more chemically stable, often present in the residual fraction of binding forms (Baran & Tarnawski, 2015; Singh et al., 2005). Soto-Varela et al. (2015) state that Al and Fe are insoluble at neutral pH, and Peng et al. (2009) show only a very acidic pH mobilises Al and Fe out of solids; since the Charlton Brook is weakly alkaline (Figs. 3 and 4), this reinforces Al and Fe's strong correlation with solid particulates.

The strong correlation coefficients for Al and Fe, both in individual and amalgamated storm events, across multiple catchment areas, highlight a consistency in their behaviour which supports the use of stormwater suspended solids to help quantify pollutant exposure and the consequent risks to benthic communities.

Manganese and Lead Manganese and lead also have strong overall correlations with suspended solids (Table 4), with all their individual correlation coefficients above 0.77, except for Storm F which has the poorest correlations for the majority of metals. Both metals have at least two gradients at a lower magnitude and the rest around 50 to 100% larger. This variation is reasonably consistent between storm events (Table 4).

Peraza-Castro et al. (2016) also show a very strong correlation between Mn and total suspended solids ($r^2=0.896$) and a moderate correlation with Pb (0.622), both comparable coefficients to those found in the Charlton Brook.

The very strong correlations between Al, Fe, Mn, and Pb (Table 3) highlight a close similarity in geochemical behaviour (Fan et al., 2021) consistent with their strong relationship to suspended solids. However, local data imply they are not from the same source. The origin of manganese is variable; Miranda et al. (2021) and Zuliani et al. (2022) highlight that Mn is abundant in the Earth's crust and is therefore likely to be lithogenic. Data collected by Reynolds (2022) show that out of all the elements studied in this report, Mn has the third largest concentration in rocks collected from around the Charlton Brook. However, Zhang et al. (2018) associate a higher concentration of Mn with increased fertiliser use, suggesting an anthropogenic source. The concentration of Mn in the rock adjacent to Charlton Brook does not show a significant difference from the UK Soil Observatory data, but Mn is elevated in the solids, with a concentration more than six times that of the soil, supporting a later anthropogenic addition of Mn into the system and an overall combined lithogenic-anthropogenic source (Reynolds, 2022; UK Soil Observatory, UKSO Map Viewer n. d.).

In contrast, lead is consistently depicted solely as an anthropogenic metal; Ateş et al. (2020) highlight traffic, agriculture, and industry as the most common sources. When comparing the average regional rock composition (which represents the natural background heavy metal concentration) to UKSO data (Reynolds, 2022; UK Soil Observatory, UKSO Map Viewer n. d.), lead within the soil is more than 6 times greater than in the rock, supporting an anthropogenic origin. The concentration of Pb in the solid

particulates is also elevated against that of the soil, although it is less significant. This would also explain why, although Pb has very strong correlations with Al, Fe, and Mn, its strongest metal correlation is with Cr, another anthropogenic metal (Miranda et al., 2021).

Anthropogenic metals are typically assigned to more mobile, exchangeable fractions, with weaker metal-solid bonding (Singh et al., 2005). Furthermore, the supply of metals from anthropogenic activities is generally more incidental than their lithogenic counterparts (Ateş et al., 2020; Burton & Johnston, 2010; Fan et al., 2021); variable point and non-point-sources from different areas of anthropogenic land use within the catchment can generate highly irregular stormwater pollutant loads (Ateş et al., 2020; Miranda et al., 2021; Song et al., 2019) and may therefore contribute to poor overall heavy metal/suspended solids correlations.

For Mn, it is possible that the consistency and stability of its lithogenic component counteracts any significant anthropogenic variability (Ateş et al., 2020; Fan et al., 2021) to maintain a very strong overall correlation with suspended solids. Fe–Mn oxides are also one of the main binding forms in solid particulates (Baran & Tarnawski, 2015), likely contributing to the strong Mn/solids correlations. Other factors have also been proposed, including solubility and pH; Madzin et al. (2015) state that Mn is more insoluble as pH increases, and Zuliani et al. (2022) couple Mn with Al and Fe, as metals which are insoluble even under oxidising conditions. When pH is around neutral, such as those in the Charlton Brook, manganese is in either the Mn(III) or the Mn(IV) oxidation state (potentially mobile fraction). Both are much less soluble than Mn(II), promoting stronger bonding with solid particulates (Soto-Varela et al., 2015).

Similar conclusions can be drawn for Pb; data collected by Baran and Tarnawski (2015) show that the fraction of readily exchangeable Pb is virtually non-existent. Instead, the majority is in the potentially mobile fraction (PMF); whether metals are retained in/on solids or become mobile is therefore dependent on the properties in the stream, including pH, temperature, oxygen availability/redox potential, and the size of carried solids (Baran & Tarnawski, 2015; Oyewo et al., 2020; Zhuang et al., 2016). Because of

Pb's very strong correlation with Mn in the Charlton Brook, the likelihood of binding with Fe–Mn oxides in solids is high. Additionally, the main source of anthropogenic lead in the catchment is from the soil (UK Soil Observatory, UKSO Map Viewer [n. d.](#)) rather than runoff and surface water outfall discharge supplied by incidental, irregular events (Burton & Johnston, 2010; Fan et al., 2021). This is likely to generate a more consistent metal input, contributing to a stronger correlation with suspended solids, even when data are combined over multiple storm events.

Zinc, Chromium, Copper, and Nickel As shown in Table 4, other heavy metals display less straightforward relationships with suspended solids. Considering zinc and chromium as examples where poorer relationships with suspended solids are obtained when all events are amalgamated, very strong correlations are obtained for some individual storms. Copper and nickel also have strong correlations for some individual storms. However, their correlations are weak when storm events are combined. For Ni, this corresponds to its strong association with PC2 rather than PC1 and SS (Figs. 5 and 7). All these metals have storm events with similar gradients, but the similarity is not consistent between all metals and between storms.

Song et al. (2019) find low average correlations between metals and total suspended solids, with weak r^2 values for Cu, Cr, Zn, and Ni, 0.13, 0.12, 0.31, and 0.02 respectively. Goldyn et al. (2018) also find extremely weak overall correlations, 0.234 for Cu and 0.291 for Zn. In the Charlton Brook, Zn and Cr are highly correlated and both have very strong correlations with Al, Fe, Mn, and Pb (Table 3), which suggests they have similar geochemical behaviour (Fan et al., 2021). Cu has a strong correlation with Zn, and Ni has a strong correlation with Cd; however, they have weak correlations with all other measured metals, exemplifying heterogeneity within the catchment. Zn, Cr, Cu, and Ni are predominantly anthropogenic metals (Miranda et al., 2021) sourced from a variety of inputs, including mining, fuel combustion, exhaust emissions, manufacturing, and some agricultural practices (Fan et al., 2021).

The anthropogenic nature of these metals in the Charlton Brook was confirmed by comparing their concentration in the river solids to their concentration in the soil (UK Soil Observatory, UKSO Map Viewer [n. d.](#)).

Research into the literature has found binding forms for these metals also vary significantly, even across individual catchment areas (Baran & Tarnawski, 2015; Oyewo et al., 2020; Singh et al., 2005). Combined with anticipated anthropogenic variability in source and supply, this heterogeneity is likely to generate unexplained variance.

Song et al. (2019) used averages of EMC, rather than amalgamating multiple data points from a single storm event to measure correlations. Furthermore, Goldyn et al. (2018) collected data at each locality over a 2-year period and used the maximum and minimum concentrations of both heavy metals and suspended solids over that time period to calculate correlation coefficients, obscuring any high correlations for individual events.

Cadmium and Beryllium As anticipated from the PCA analysis, cadmium and beryllium have very weak overall correlations with suspended solids. Cd has moderate correlations with suspended solids in Storm C and Storm B and Be in Storm A, but all other individual storm correlations are weak (Table 4).

Cd and Be have a moderate correlation with each other (Table 3). Cd also has a strong correlation with Ni, and Be has a moderate correlation with Ni. However, they show weak correlations with all other measured metals.

Be and Cd are anthropogenic metals commonly sourced from the electrical industry (Fishbein, 1981; Fan et al., 2021), and their weak correlation with suspended solids indicates weak metal-solid bonding, regardless of variability between storm events. This suggests that Cd and Be have high mobility, associated with weaker, readily exchangeable binding forms, and are minimally affected by changes in environmental conditions. This is supported by Zhuang et al. (2016), who record the largest fractions of Be as exchangeable and carbonate bound. Data collected by Huang et al. (2017) show Cd is very naturally mobile and has a high concentration ratio of dissolved cadmium versus cadmium in the solids.

The storm data intercepts are of low magnitude and vary, suggesting changes in background concentrations (Table 4); Miranda et al. (2021) state that elements in low concentrations compared to other heavy metals, like Cd and Be, often face competition for bonding with solid particulates, irrespective of their preferred binding form. Therefore numerous factors can be attributed to the weak relationship between Cd, Be, and suspended solids.

3.2.4 ANCOVA Results

The variability in metal concentrations between storm events, highlighted by the PCA and linear regression, is analysed further using ANCOVA to determine whether any difference in mean metal concentration between storm events is significant, whilst statistically accounting for both the concentration of suspended solids and the interaction effect between storm event and suspended solids. Levene's test for the homogeneity of variance indicates significant differences for all metals apart from Al and Pb; this is expected as the range of suspended solids concentrations for a storm varies considerably between storms. Whilst acknowledging these departures from test prerequisites, including homogeneity of all regression slopes, significant differences are observed for all metals, apart from Be and Cd. Table 5 is aligned with the transformed PCA results, which indicate data for Storms C, D, E, and F are clustered together (Fig. 5d). Storms C and E are similar for the largest number of metals, corresponding to their shared association with PC1.

Even for metals such as Al and Fe that have very strong overall storm correlations (>0.9), not all storm events are significantly similar. In contrast, although no significant relationship between Ni and SS is shown in the correlation matrix (Table 3), significant differences are observed for Ni here where the storm event is a factor.

This brings forward inherent problems — should storm data be combined when storm events are significantly different, and should the overall relationship between suspended solids and heavy metals still be used to predict reliable pollutant loads? These results highlight the importance of using data measured from individual storm events in the prediction of reliable pollutant loads, particularly with anthropogenic metals, which show a larger natural variability.

3.3 Limitations

The variation between storms highlighted by linear regression and ANCOVA are unaccounted for; to assess the biotic exposure to these metals accurately, especially those which do not behave consistently with suspended solids, further work may be required to understand the variability in pollutant/solids relationships, which likely results from changes in environmental variables that were not measured.

The water chemistry is primarily controlled by the regional geology, hydro-meteorology, and seasonal changes within the catchment and has the potential to affect the metal concentration (Aleksander-Kwaterczak & Plenzer, 2019). DOC (dissolved organic carbon), which was not measured for this study, impacts the adsorption and desorption of heavy metals from the surface of solids and their solubility, hence affecting the measured metal concentration (Fan et al., 2021; Hergren et al., 2005; Soto-Varela et al., 2015). The quantity of organic matter is also thought to alter oxygen demand which impacts metal bioavailability and consequently, their concentration in solids (Burton & Johnston, 2010; Komínková, 2012); COD has a strong to moderate correlation with Fe, Al, Zn, Pb, Mn, Cu, and Cr (Table 3) and a significant loading with PC1 (Table 2), which suggests COD has an impact on metal concentration in the Charlton Brook. The presence of suspended oxides and phosphorous compounds in the water column also encourages bonding with

Table 5 The similarity of mean metal concentration between storms using post hoc Tukey tests, accounting for suspended solids and interaction effects

Storm	A	C	D	E	F
A	–	Cu, Zn	Cr, Cu, Mn, Zn	Cu, Fe, Mn	Cu
C		–	Al, Cu, Fe, Zn	Al, Cr, Cu, Fe, Ni, Pb, Zn	Cr, Cu, Pb, Zn
D			–	Al, Cr, Cu, Fe, Mn	Cu, Ni
E				–	Cu, Cr, Pb, Zn
F					–

metals (Miranda et al., 2021). Therefore, water chemistry has the potential to greatly impact pollutant/solids correlations. A higher stormwater discharge, transporting a coarser solid load, can also reduce the correlation between metals and solids due to a reduced carrying capacity (Peraza-Castro et al., 2016).

Furthermore, the time period of data collection, which was over 5 months, does not allow for the full effect of seasonality. Hallberg et al. (2007) suggest the correlation between suspended solids and heavy metals may be greater in the winter months. The seasonal variability in rainfall quantities, which can lead to intermittent heavy metal dilution (Deng et al., 2018), also has the ability to alter the heavy metal/suspended solids relationship.

Therefore, developing a more detailed understanding of how the relationship between suspended solids and heavy metals varies will help to improve the accuracy of pollutant exposure modelling over the lifecycle of benthic organisms; this will require the collection of large amounts of data with a shorter sampling frequency, during storm events, rather than relying on EMCs and long-term concentration averages. A larger reference dataset from small stream catchments will also improve pollutant exposure models by incorporating a wider variability in macroinvertebrate assemblages.

3.4 Applications

From the results of this paper, it is envisaged the data can be used in the following way: once the transport of suspended solids driven by storm flows can be modelled accurately within specific catchment areas, then linear regression equations can be utilised to generate pollutant loads for single or multiple events (if storm events are statistically similar).

Once pollutant loads have been more accurately modelled, they can be compared to ecological standards. For example, for the storms measured here in the Charlton Brook, four and six of the seven sampled storms exceeded the 1-h Criteria Maximum Concentration (United States Environmental Protection Agency (USEPA), 1986) for Al and Cu respectively (Robson et al., 2006). Macro-invertebrate pollutant exposure can also be assessed from an individual or a combination of metal loads in a variety of catchments, as well as the metal exposure of treatment ponds being designed to remediate stream water quality. A greater understanding of the relationship between suspended solids and metal

contaminants is also extremely important for assessing bioavailability (Carter et al., 2006). The bioavailability and ecological toxicity of the metals must be considered and used to evaluate the threat to benthic organisms in order to assess the scale of remediation required (Burton & Johnston, 2010; Miranda et al., 2021).

The collection of reliable data also contributes to improving the prediction of stormwater pollution loads by increasing the quantity of data available to input into water quality models. The lack of water quality data from individual storm events has also limited modelling in the past. Although models cannot be a perfect representation of reality, incorporating more detailed data, collected during storm events will help to incorporate the natural variability of urban drainage basins and predict pollutant exposures with improved reliability (Bertrand-Krajewski, 2007; Vaze & Chiew, 2003).

The relationship between suspended solids and heavy metals also has applications in other analogous fields:

In a recent study in urban lakes by Rajasekar et al. (2022), the emergence of specific antibiotic genes correlates with anthropogenic metals. However, only surface water samples were collected; when more than 90% of heavy metal loads in aquatic systems are related to solid particles (Zhang et al., 2014), this demonstrates a gap in research where the relationship between suspended solids and heavy metals could be employed to investigate a future risk to human life.

In addition to urban streams, it is also important to monitor pollutant loads in marine settings, particularly around extremely vulnerable ecosystems like coral reefs, which are increasingly under threat from human activity (Dehno et al., 2022). However, before using solids as a proxy for heavy metal exposure, the impact of freshwater versus saltwater on the absorption of pollutants onto the solid particulate surface needs to be assessed.

The re-suspension of solids within reservoirs has also been identified as a major source of water pollution, triggered by thermal stratification or physical disturbance. The relationship between heavy metals and solids within 'slow-flow water bodies' is an emerging area of research, likely associated with concerns for future water security (Zhang et al., 2022). Relative to fast-flowing streams, where solids are regularly exposed to medium-high-speed disturbances, the effect on pollution levels will vary significantly with intermittent, low-velocity disturbance in a reservoir (Peng et al., 2021); as long as this

variability is accounted for, applying the relationship between heavy metals and suspended solids for monitoring water quality has much wider applications.

4 Conclusions

This study examines pulse exposures of chemical stresses to benthic communities during frequent storm events in a small, urbanised catchment — a type that is normally neglected and whose contribution to the quality of larger catchments is overlooked. As routine sampling campaigns are limited in extent, this work assesses the use of suspended solids concentrations as an environmental indicator of the episodic heavy metal pollution of benthic communities. Thus, the key question is, do reliable and consistent relationships between these variables exist?

Principal component analysis confirms a strong association of most heavy metal concentrations with suspended solids. There is a weaker association with discharge; storm data exhibit early peaks of both runoff and maximum solids concentrations originating from stormwater sewers in the urbanised lower reaches, followed by slower less turbid rural runoff.

A correlation matrix using combined event data shows a strong relationship between metals and suspended solids concentrations for lithogenic Fe and Al, which weakens in the order Mn, Zn, Pb, Cr, and Cu, reflecting increasing anthropogenic origin. The correlation coefficient for Ni, Be, and Cd is poor.

Linear regression indicates some metals (e.g. Fe, Al, and Mn) are strongly correlated with solids for both individual and pooled storms; for others (e.g. Cu and Ni), a strong correlation is observed for some events but is poor when storms are amalgamated. Analysis of covariance also shows the behaviour of an individual metal is the same in some storms but not others and that the pattern is not consistent between metals. Experimental variation must therefore be accepted, particularly for metals' influenced by anthropogenic activity. Resolving unexplained variance in the storm data requires further research.

This work signifies the use of suspended solids as a surrogate water quality indicator has strong indicative potential in determining the pollutant load from one or more of the metals by application of linear regression equations to suspended solids, for single or multiple statistically similar events. A greater account

of metal concentration variations will result in more accurate modelling of pollutant exposure, such as over the lifetime of macro-organisms, which would also be improved by a wider reference data set from small catchments. This will assist in determining the scale and type of remediation that is required.

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Data Availability The datasets from this study are available on reasonable request.

Declarations

Conflict of Interest The authors declare no competing interests.

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